Phys 344

Lecture 28.

Phase Transition

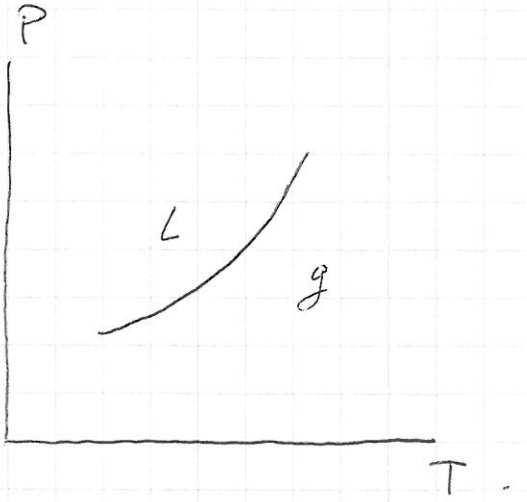
Assignment #10.

5.28, 30, 32, 35, 36.
48, 51.

- The Clausius-Clapeyron Relation.

On the phase boundary in (P, T) space.

L a line $P = P(T)$.



along that line,

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

L — latent heat.

$\Delta V = V_g - V_\ell$.

} for 1 mol. (OR. for 1 kg).

e.g. H_2O: when $P = 1 \times 10^5$ Pa

$T = 100^\circ C = 373$ K

$L = 2.26 \times 10^6$ J/kg

$V_\ell = 1.04 \times 10^{-3}$ m^3/kg

$V_g = 1.7$ m^3/kg. $(V_g \gg V_\ell)$

find $\frac{dP}{dT}$: $\frac{dP}{dT} = \frac{2.26 \times 10^6}{373\,(1.7 - 1.04\times10^{-3})} = 3.57 \times 10^3$ Pa/K.

e.g. In an autoclave (steriliser), the pressure is 200 kPa, what is the boiling temperature of water under this pressure?

$$\frac{\Delta P}{\Delta T} = 3.57 \times 10^3$$

$$\frac{2 \times 10^5 - 1 \times 10^5}{T - 373} = 3.57 \times 10^3$$

$$T = 373 + \frac{10^5}{3.57 \times 10^3} = 401\ K = 128\ ^\circ C$$

- Derivation of Clausius-Clapeyron relation

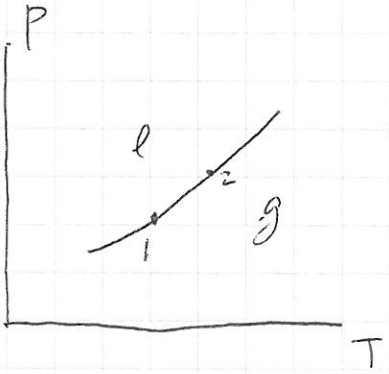
Consider 1 mol of gas and 1 mol of liquid.

$\mu_\ell = \mu_g$.

$G_\ell = G_g$ at phase boundary.

equilibrium.

$dG_\ell = dG_g$.



$$-S_\ell\, dT + V_\ell\, dP = -S_g\, dT + V_g\, dP$$

$$\therefore \frac{dP}{dT} = \frac{S_g - S_\ell}{V_g - V_\ell} = \frac{L}{T(\Delta V)}$$

$$\Delta V = V_g - V_\ell \approx V_g$$

Note: can be applied to any 2 phases. (Besides gas-liquid).

e.g. Diamond and Graphite.

Carbon : C.

2 solid phases : diamond cubic - 8 atoms.
(different structures) graphite. layered hexagonal.

Gibbs free energy under standard condition. (1 atm = 10^5 Pa. Room Temp = 298K)

$G_d = 2.9$ kJ

$G_g = 0$.

∴ under standard condition, graphite is more stable than diamond.

That's why it's so much easier to make graphite than diamond.

However, $V_g = 5.3\ cm^3$, $V_d = 3.42\ cm^3$.

$\therefore \quad V_g > V_d$.

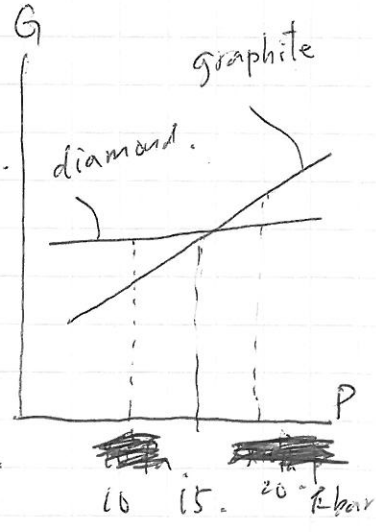
$$\left(\frac{\partial G}{\partial P}\right)_T = V > 0.$$

when P increases, G_g increases faster than G_d.

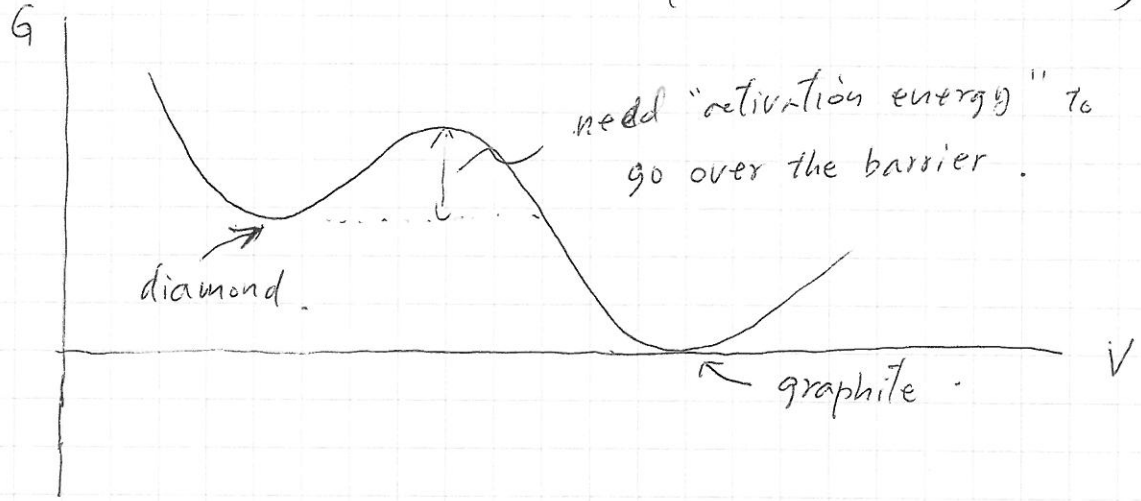
at about 15 kBar, $G_g = G_d$.

15,000 atm. — very high pressure

(50 km depth of rock)



• Question: Why doesn't diamond spontaneously convert to graphite ?
(under standard condition)



"activation energy" ~ 1500°C. at 1atm.

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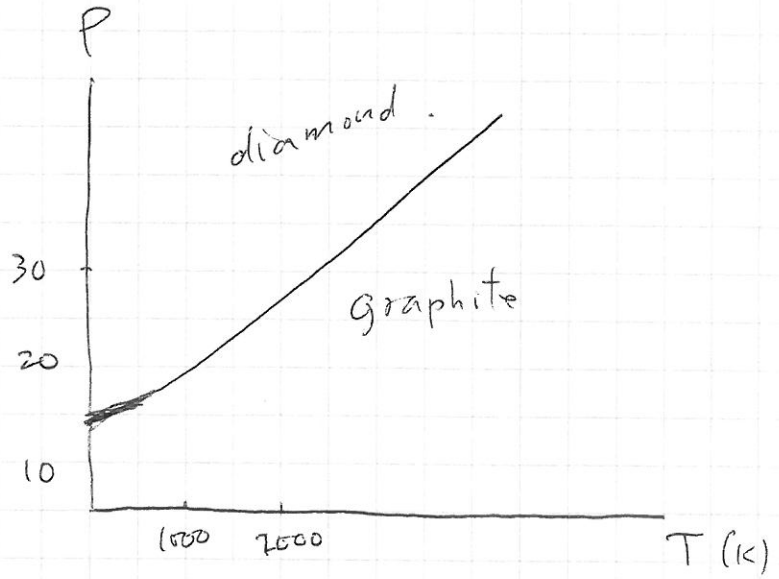
phase diagram:



slope of boundary:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{S_g - S_d}{V_g - V_d}.$$

$$= \frac{5.74 - 2.38}{5.30 - 3.42}$$

$$= 1.8 \times 10^6 \ Pa/K.$$

(near standard condition).